

**VOLCANIC AEROSOLS:  
CHEMISTRY, MICROPHYSICS, EVOLUTION AND EFFECTS**

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## Introduction

Stratospheric aerosols have been the subject of scientific speculation since the 1880's, when the powerful eruption of Krakatoa attracted worldwide attention to the upper atmosphere through spectacular optical displays. The presence of a permanent tenuous dust layer in the lower stratosphere was postulated in the 1920's following studies of the twilight glow. Junge collected the first samples of these 'dust' particles and demonstrated that they were actually composed of sulfates, most likely concentrated sulfuric acid (Junge and Manson, 1961; Junge, 1963). Subsequent research has been spurred by the realization that stratospheric particles can influence the surface climate of earth through their effects on atmospheric radiation. Such aerosols can also influence, through chemical and physical effects, the trace composition of the atmosphere, ozone concentrations, and atmospheric electrical properties.

The properties of stratospheric aerosols -- both the background particles and those enhanced by volcanic eruptions -- have been measured in situ by balloon ascents and high-altitude aircraft sorties. The aerosols have also been observed remotely from the ground and from satellites using both active (lidar) and passive (solar occultation) techniques (remote sensing instruments have been carried on aircraft and balloon platforms as well). In connection with the experimental work, models have been developed to test theories of particle formation and evolution, to guide measurement strategies, to provide a means of connecting laboratory and field data, and to apply the knowledge gained to answer practical questions about global changes in climate, depletion of the ozone layer, and related environmental problems.

Figure 1 illustrates the various kinds of aerosols that have been identified in the stratosphere. The figure provides information on the size dispersion and concentration of these diverse particulates.

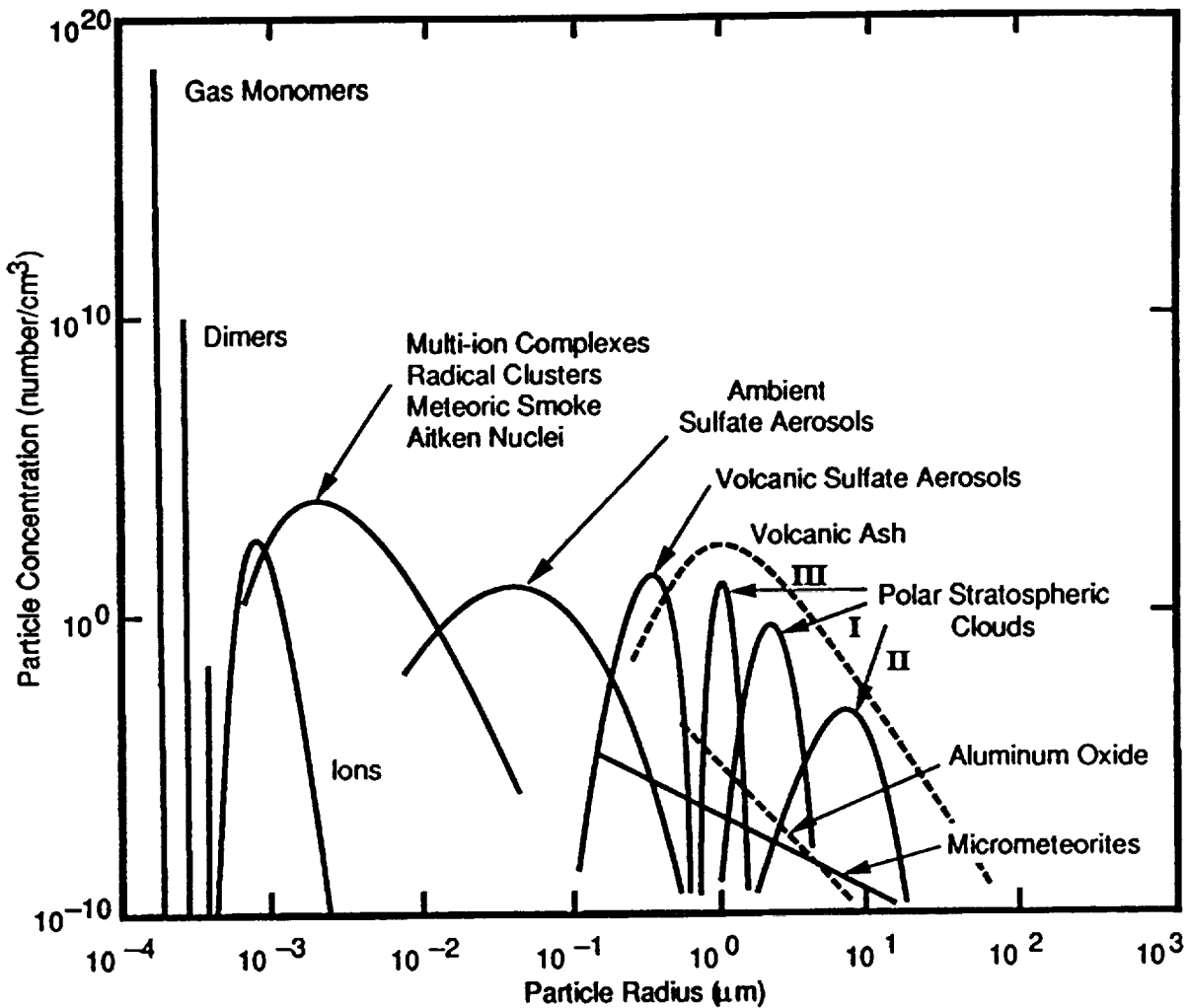


Figure 1. Spectrum of particles in the earth's stratosphere. Shown are the approximate size dispersions of particles of different origin. The total number concentration of each type of particle is roughly indicated by the peak value on the vertical scale. Some aerosols are highly variable in concentration and properties, particularly the 'volcanic ash' component of volcanic eruption clouds; typically, these particles will fall out of the stratosphere within a few months of an eruption.

## Stratospheric Sulfate Aerosols and Precursor Gases

The environmental conditions that exist in the stratosphere favor the formation of sulfuric acid aerosols in the presence of sulfur-bearing precursor gases. Because such gases exist in the background atmosphere, the stratosphere always contains a tenuous, ubiquitous sulfate haze. The processes that control this haze also control the formation and evolution of volcanically-induced aerosols. Accordingly, investigations of the ambient stratospheric aerosol layer provide insights into the behavior of volcanic eruption clouds above the tropopause.

### Background Aerosols

It is now fairly well established that the ambient stratospheric sulfate layer is formed as a result of the chemical transformation and condensation of sulfur-bearing gases (OCS, SO<sub>2</sub>) transported into the stratosphere from the troposphere or injected there by large volcanic eruptions. The general properties of these aerosols are summarized in Table 1.

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**Table 1. Properties of Stratospheric Sulfate Aerosols**

Composition -- H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O (~70%/30%); Traces of sulfates, nitrates, nitryls, chlorides

Origin -- Tropospheric sulfides; OCS, CS<sub>2</sub>; Volcanic sulfur emissions; SO<sub>2</sub> photochemical oxidation to H<sub>2</sub>SO<sub>4</sub> via OH

Properties -- Liquid spheres, perhaps slurries and some solids; < 1 ppbm; ~1/cm<sup>3</sup>, ~ 0.1 μm radius

Distribution -- Global; 12 to 30 km altitude; Latitudinal and seasonal variations

Effects -- Shortwave radiation scattering (τ < 0.01); Longwave absorption/emission (τ << 0.01); Heterogeneous chemical activation of chlorine (?)

Influences -- Natural and anthropogenic OCS sources; Volcanic activity; Stratospheric dynamics

Trends -- Global increase of ~ 6%/yr in mass

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In addition to the chemical reactions of precursor sulfur gases -- which are illustrated in Figure 2 -- that lead to the production of condensible sulfur compounds -- primarily  $\text{H}_2\text{SO}_4$  -- evolution of the sulfate particle layer involves a number of microphysical processes; these include aerosol nucleation, growth by condensation, evaporation of volatiles, coagulation, and gravitational sedimentation.

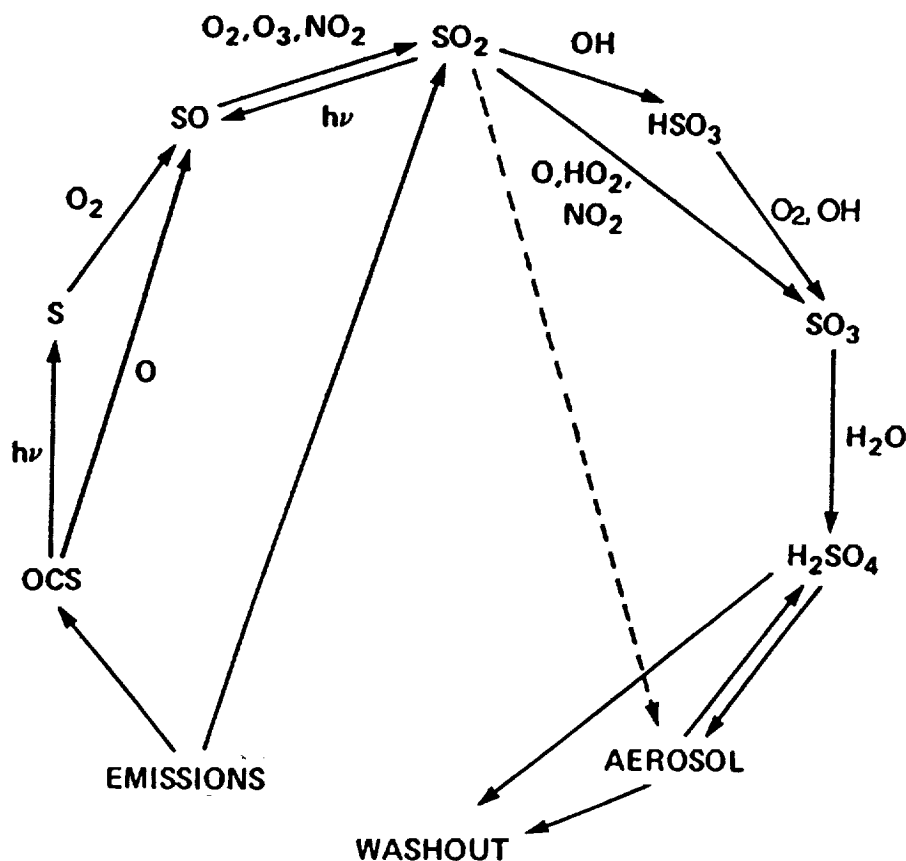


Figure 2. Gas phase sulfur reaction pathways that lead to the production of sulfuric acid vapor, which condense to form sulfate aerosols. The reactions are essentially irreversible in the lower stratosphere, and sulfur is ultimately lost through transport of stratospheric aerosols into the upper troposphere. In the upper stratosphere, enough ultraviolet radiation is present that  $\text{H}_2\text{SO}_4$  may be photodissociated, thus recycling sulfur into simpler forms (however, the  $\text{H}_2\text{SO}_4$  photodissociation rate has never been measured).

Some of the complex physicochemical processes responsible for the formation of the stratospheric aerosol layer are illustrated schematically in Figures 3 and 4. The potential contribution of meteoritic debris and ion clusters in sulfate particle formation are also indicated in Figure 4.

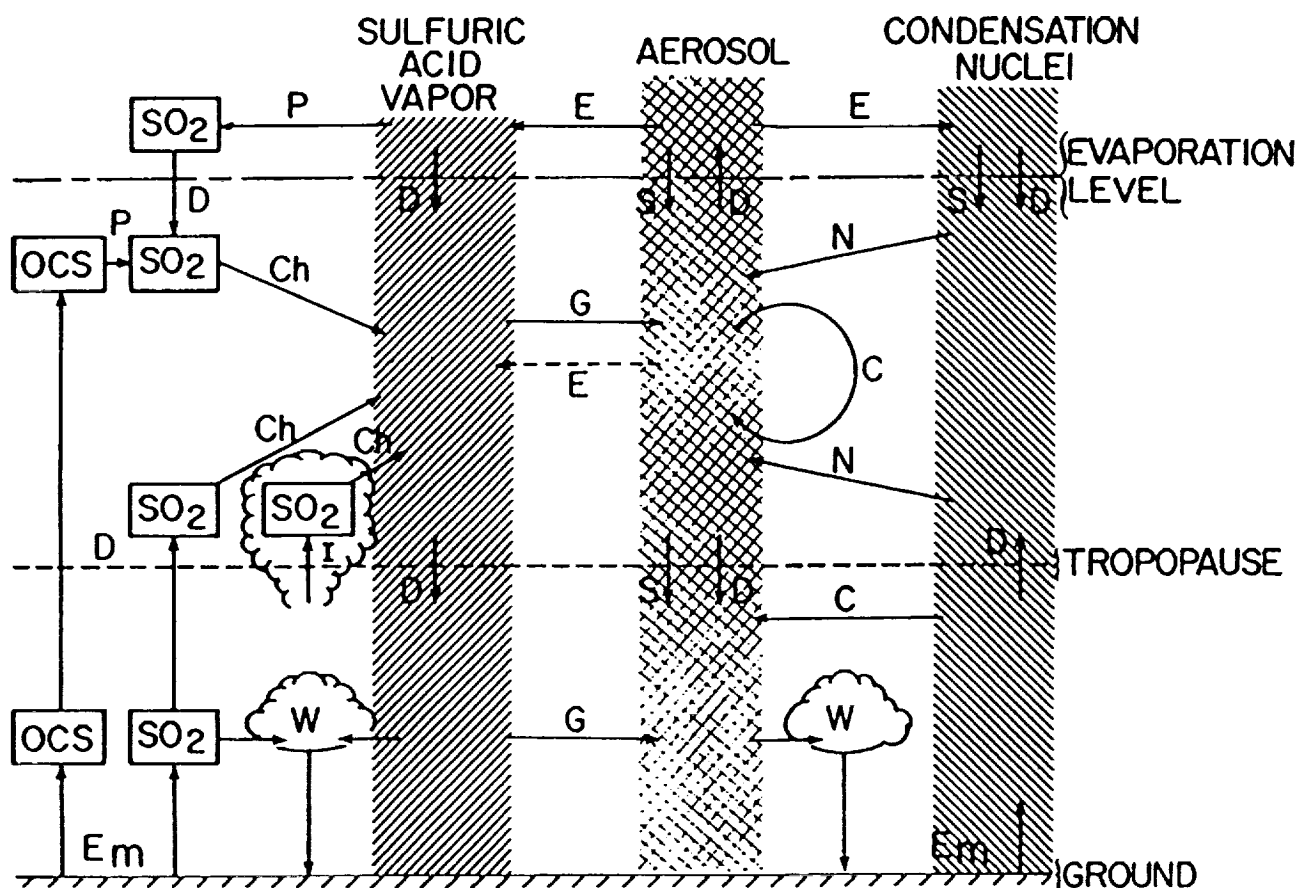


Figure 3. Schematic diagram of the microphysical and chemical processes that control the formation and evolution of stratospheric sulfate aerosols. The principal compositional elements are: precursor sulfur-bearing gases; sulfuric acid vapor; condensation (Aitken) nuclei; and sulfate aerosols. The letters represent specific processes and interactions: C = coagulation, Ch = chemical reaction, D = diffusion (turbulent), E = evaporation, Em = emission, G = growth by condensation, I = injection (e.g., by volcanic eruptions), N = nucleation, P = photolysis, S = sedimentation, and W = washout.

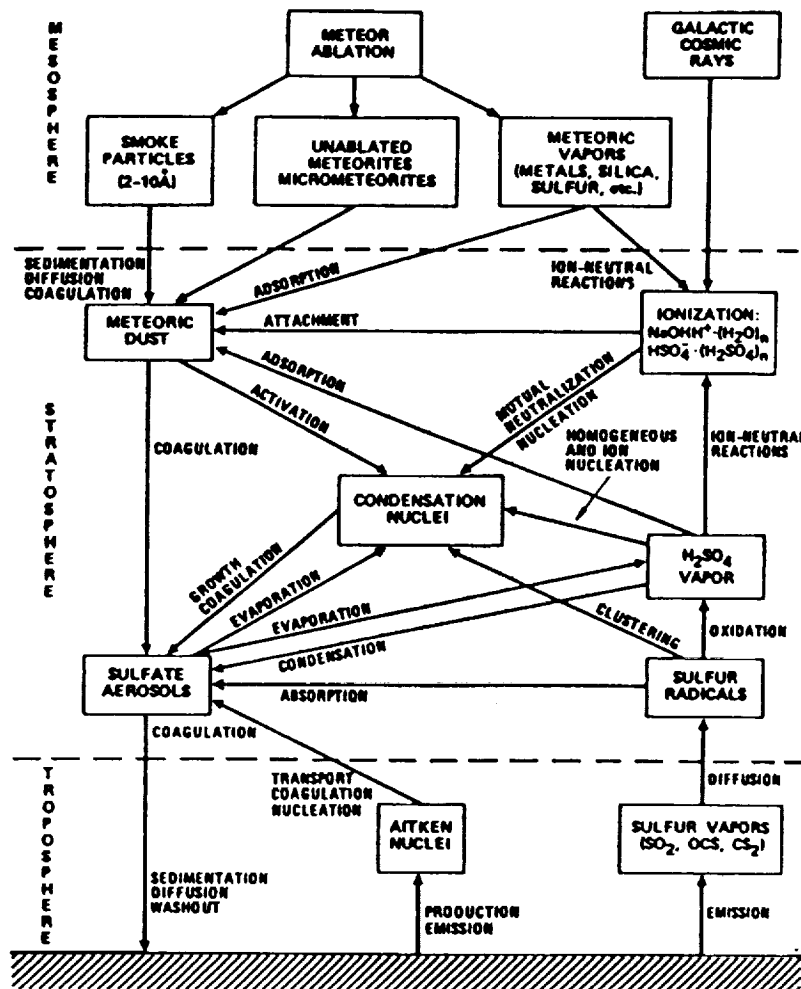


Figure 4. Diagram depicting the physical and chemical processes which affect stratospheric aerosols. Meteoritic debris, positive and negative ions, and tropospheric Aitken nuclei can serve as nucleation sources for sulfate aerosols and ice clouds. These particles can grow, evaporate, coagulate and fall vertically. The particles are also advected in stratospheric winds and diffuse under the influence of small scale turbulent eddies.

## Volcanic Aerosols

Table 2 summarizes the general properties of the sulfate aerosols generated by a large volcanic eruption (that is, one for which the eruption column penetrates the tropopause and deposits substantial quantities of gaseous and particulate emissions in the stratosphere).

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**Table 2. Properties of Volcanic Aerosols**

Composition -- Silicates;  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  (~70%/30%); Traces of sulfates, nitrates, chlorides, etc.

Origin -- Volcanic  $\text{SO}_2$  fumes;  $\text{H}_2\text{S}$ ?, OCS,  $\text{CS}_2$ ; Photochemical oxidation to  $\text{H}_2\text{SO}_4$  via OH

Properties -- Liquid spheres; Solid mineral particles dominant the first month;  
~ 100-1000 ppbm; (highly variable); ~1-10/cm<sup>3</sup>; ~ 0.3  $\mu\text{m}$  radius

Distribution -- Regional (days); Zonal (weeks); Hemispheric (months); Global (year)

Effects -- Shortwave radiation scattering ( $\tau > 0.1$ ) leads to surface cooling;  
Longwave absorption warms the stratosphere;  
Injection of HCl,  $\text{H}_2\text{O}$ , etc., alter air composition;  
Heterogeneous reactions on sulfate aerosol surfaces;  
Ozone decrease from  $\Delta T$ ,  $\Delta \text{HCl}$ ,  $\Delta \text{Aerosol}$ , etc.;  
Stratospheric stability / tropospheric dynamics affected;  
Nuclei for upper tropospheric cirrus (?)

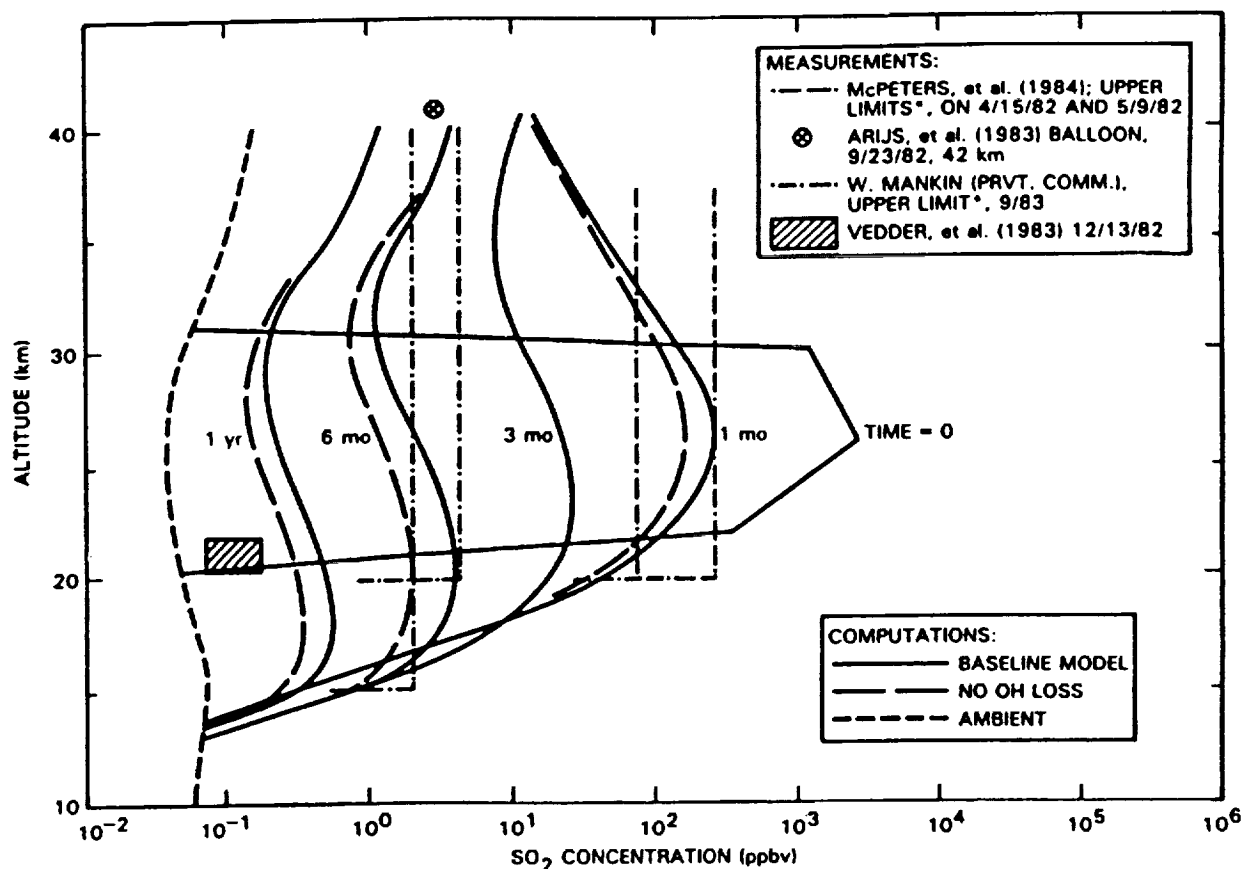
Influences -- Geophysical; No anthropogenic influences; Geological setting determines effects;  
Impact on ozone affected by future CFC buildup

Trends -- Significant eruption every ~20 years on average; Major eruptions are ~100 years apart

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The microphysical development and properties of volcanic eruption clouds can be illustrated through model simulations that include all of the relevant physical and chemical processes (Turco et al., 1982, 1983; also see Figures 2-4). In the following series of figures, simulations of the evolution of the El Chichon eruption cloud are used to indicate the behavior of volcanic aerosols. The primary eruption of El Chichon occurred on April 4, 1982; debris and gases were injected to altitudes of about 30 km over the Yucatan peninsula.

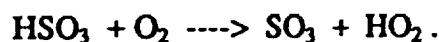




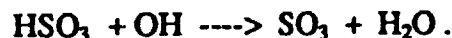
\* ASSUMING THAT THE  $\text{SO}_2$  IS UNIFORMLY MIXED ABOVE THE LEVEL INDICATED

Figure 5. Simulation of the El Chichon volcanic eruption cloud  $\text{SO}_2$  concentration using a one-dimensional aerosol/photochemistry model. The initial  $\text{SO}_2$  injection profile (reconstructed from sparse data defining the injection heights) is shown, along with vertical profiles during the first year following the eruption. Some data on observed  $\text{SO}_2$  concentrations are plotted.

Figure 5 illustrates the vertical diffusion of the initially-injected  $\text{SO}_2$  over time, and the  $\text{SO}_2$  depletion by chemical transformation into  $\text{H}_2\text{SO}_4$ . Two depletion scenarios are shown. The results corresponding to "NO OH LOSS" are probably the more accurate, although the differences between the simulations shown are relatively small. These results seem to fit the limited constraints imposed by the few direct  $\text{SO}_2$  concentration measurements available. The "NO OH LOSS" computation includes the key sulfur reaction,



The reaction is so rapid that sulfur radicals (i.e.,  $\text{HSO}_3$ ) never achieve a significant concentration, and thus do not play a role in the chemical evolution of the aerosol cloud (except as an intermediary sulfur species). More importantly, this reaction does not consume odd-hydrogen,  $\text{HO}_x$ , as would the competing process,



Hence,  $\text{HO}_x$  is not consumed as it proceeds to oxidize  $\text{SO}_2$  catalytically.

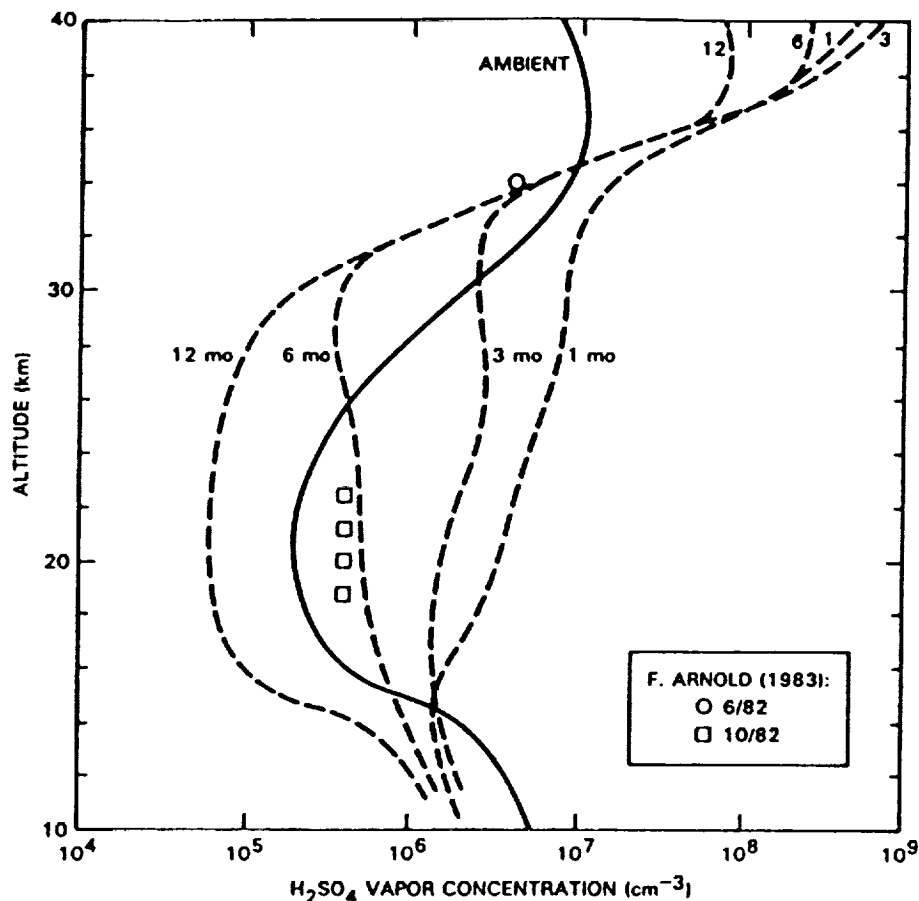


Figure 6. Sulfuric acid vapor concentrations resulting from the oxidation of  $\text{SO}_2$  injected by El Chichon (as described in Figure 5). Some observational data are compared. The ambient  $\text{H}_2\text{SO}_4$  profile is shown for comparison (the ambient profile comes from a model that has been validated against measurements; Turco et al., 1982).

The  $\text{H}_2\text{SO}_4$  concentrations exhibit an interesting behavior. At early times, the concentrations increase, which would be expected as excess  $\text{SO}_2$  injected by the volcano is oxidized. However, at late times, the  $\text{H}_2\text{SO}_4$  concentrations fall even below the ambient concentrations. The depletion occurs because the mass (and surface area) of the sulfate aerosols has increased substantially during this period (and will remain elevated for at least two years). The rate of  $\text{H}_2\text{SO}_4$  vapor deposition (and loss) is roughly proportional to the aerosol surface area at any time. The maximum increase in  $\text{H}_2\text{SO}_4$  vapor -- a factor of about 10 -- is limited by condensation. As can be seen in Figure 7, the maximum increase in sulfate mass is much greater for this case -- about a factor of 100.

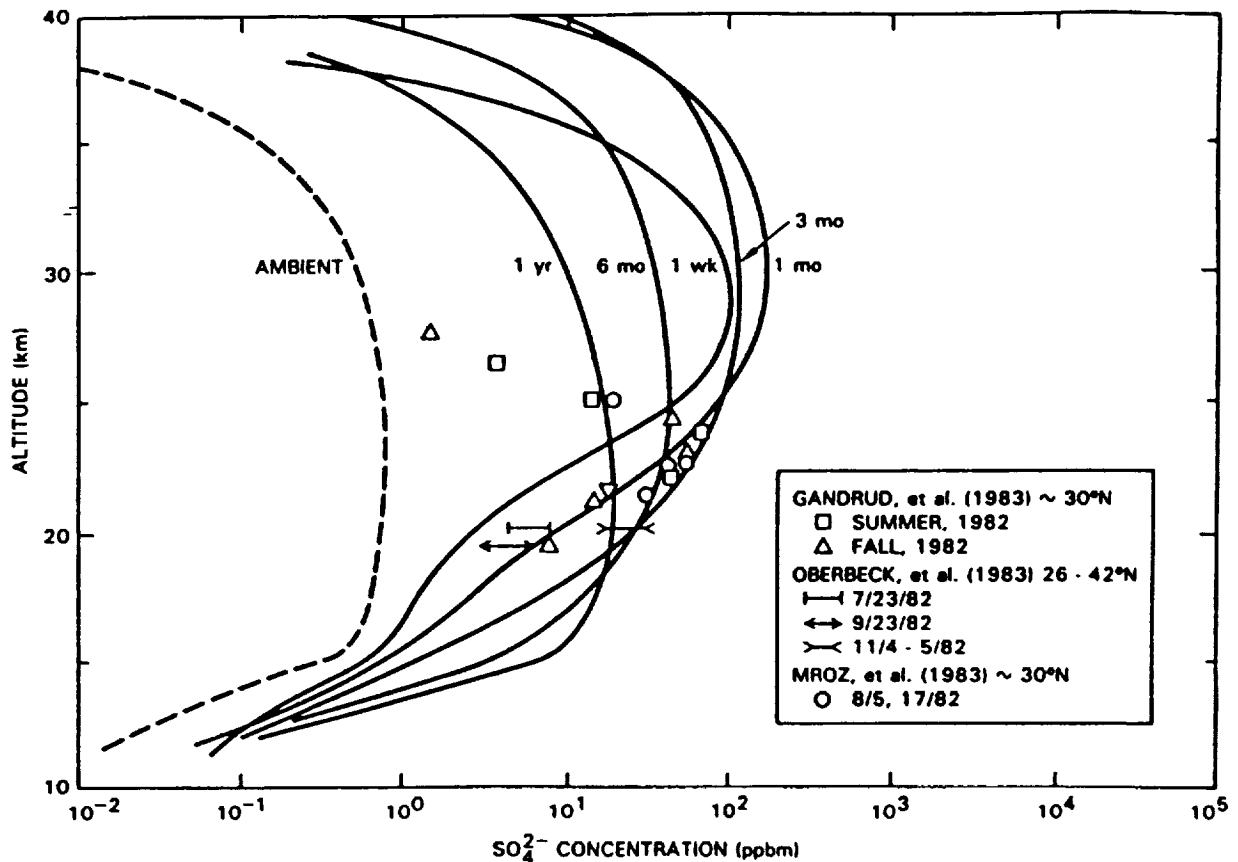
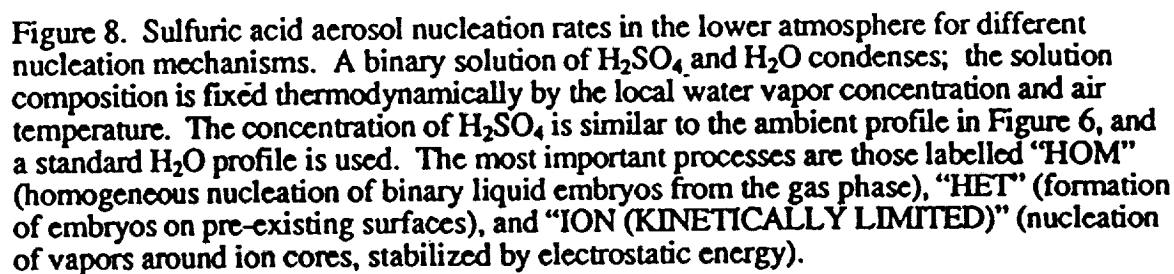


Figure 7. Sulfate mass concentrations (expressed in parts per billion by mass) are illustrated for the conditions corresponding to Figures 5 and 6. Data are compared. The ambient (computed) aerosol mass profile is also shown. The predicted mass profiles are shown at various times following the eruption.

The predicted aerosol sulfate mass profiles in Figure 7 compare favorably with observations below about 25 km, but overestimate the mass above this altitude, indicating a substantial aerosol burden up to about 40 km. It should be noted that high-altitude sampling of the volcanic clouds was very limited. Data collected by the Solar Mesosphere Explorer satellite suggest, indeed, that the aerosols of El Chichon reached altitudes of 40 km (Watson et al., 1990). However, the assumptions concerning vertical 'eddy' diffusion explicit in the one-dimensional model used in this study clearly causes the sulfur gases and aerosols to be transported too rapidly above 25 km. Lidar measurements indicated that the El Chichon particles remained below about 30 km for several months following the eruption. A point to note is that, although the aerosol mass mixing ratio is relatively large above 30 km, the absolute sulfate mass is relatively small.



It is important to note that, in the ambient stratosphere, nucleation rates that exceed about  $10^{-6}/\text{sec}$  are significant because, over time, aerosol concentrations of  $\sim 1/\text{cm}^3$  can accumulate. In the lower stratosphere, water vapor abundances are high enough and temperatures are cold enough that homogeneous nucleation can occur if the  $\text{H}_2\text{SO}_4$  concentration is well above ambient. If the peak  $\text{H}_2\text{SO}_4$  vapor concentrations in the core of a volcanic cloud exceed those in Figure 6, homogeneous nucleation can proceed rapidly and aerosol concentrations would be dominated by newly formed particles.

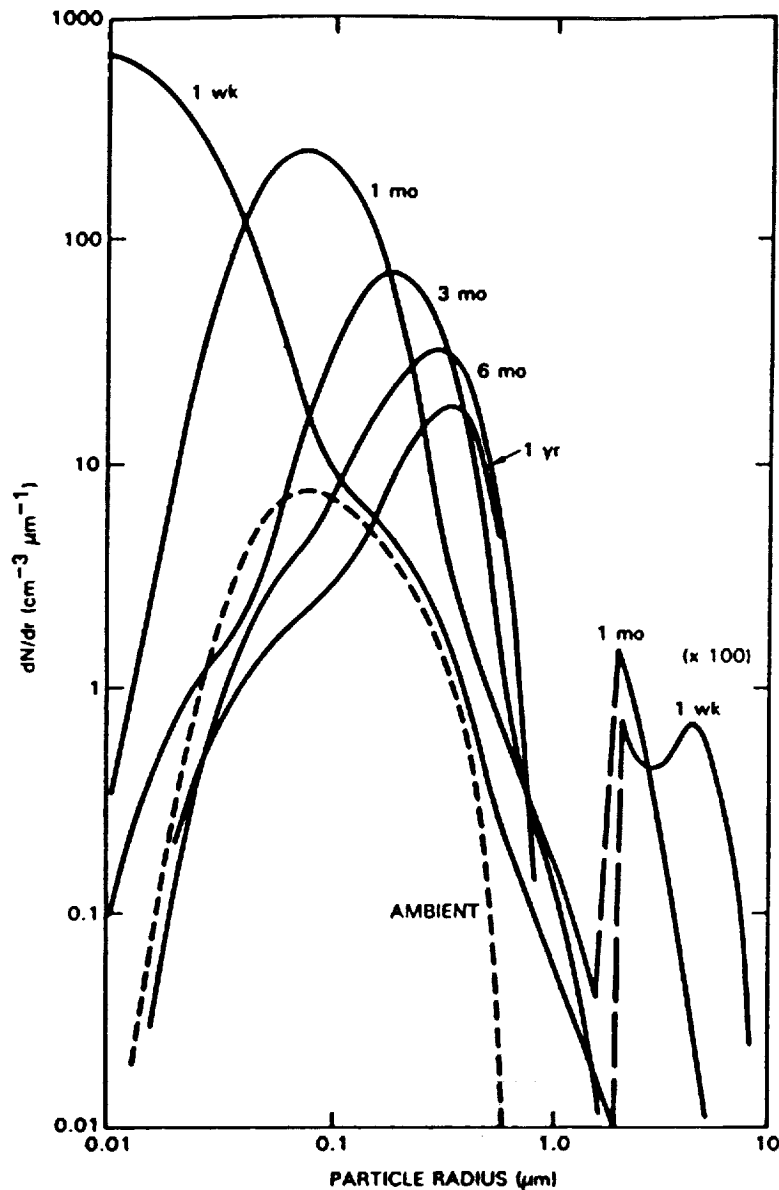


Figure 9. Evolution of the aerosol size distribution at 20 km in the simulated El Chichon eruption cloud. Size distributions are shown at early and late times, and are compared to the ambient size distribution.

The simulated size distributions of volcanic aerosols in Figure 9 exhibit a tri-modal structure that varies over time. The principal modes are: nucleation mode, which is most prominent at early times and at sizes near  $0.01 \mu\text{m}$ ; sulfate accumulation mode, which evolves initially from the nucleation mode (by coagulation and condensation) and increases in size to about  $0.3 \mu\text{m}$  after one year; large-particle 'ash' mode (of solid mineral and salt particles) that settles out of the layer within the first month. A primary feature of the volcanic aerosol size distribution after several months is a greatly enhanced sulfate accumulation mode. The mass residing in this mode is indicated in Figure 7. The increased aerosol size is caused by an accelerated growth rate in the presence of enhanced sulfuric acid vapor concentrations maintained by  $\text{SO}_2$  chemical conversion.

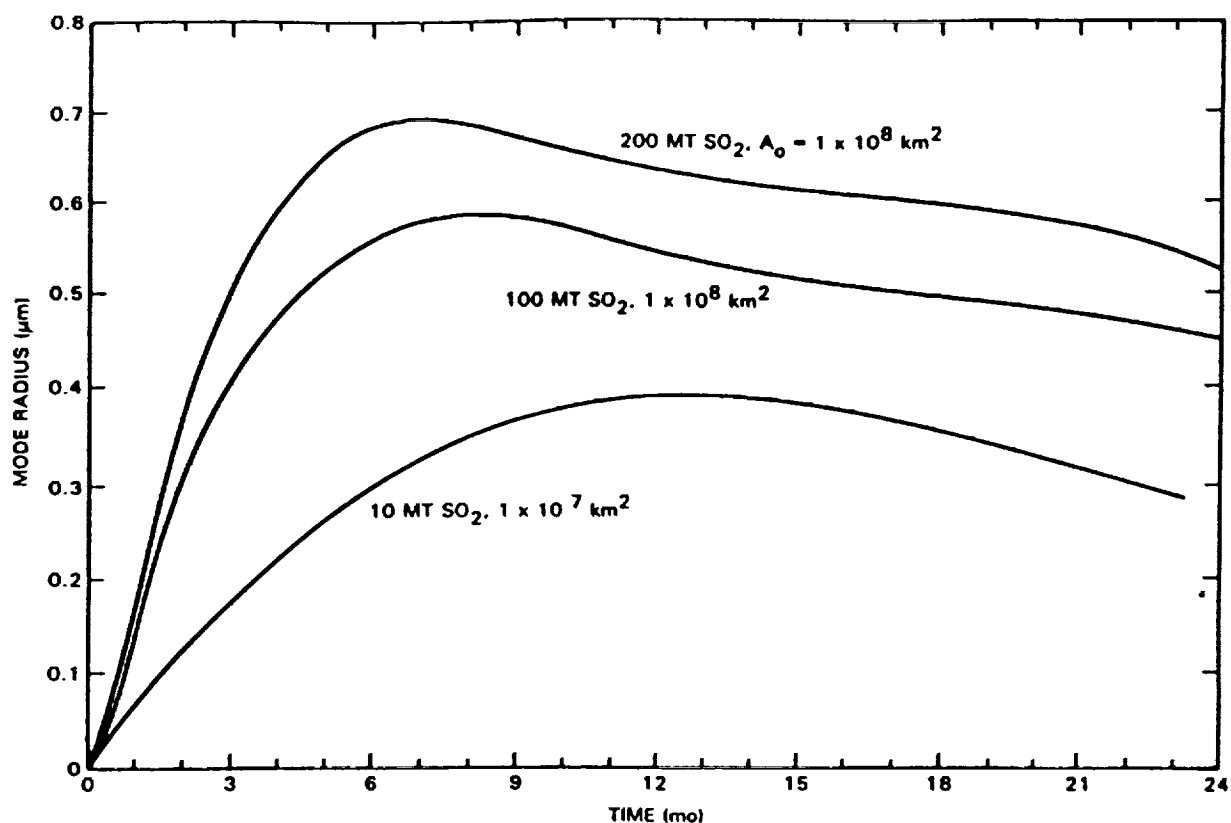


Figure 10. Mode radius of an equivalent log-normal size distribution that fits the computed sulfate accumulation mode versus time in a volcanic eruption cloud. The  $\text{SO}_2$  injections that correspond to these simulations are indicated on the figure in megatons (MT) or  $10^6$  metric tons. The area,  $A_0$ , is the initial area over which the volcanic debris is assumed to be distributed; the cloud subsequently expands horizontally over the globe, with an equivalent horizontal diffusion coefficient of  $1 \times 10^{11} \text{ cm}^2/\text{sec}$ . Note that the mode radius approaches zero at early times in these simulations because of the large number of extremely small freshly-nucleated particles. (Pinto et al., 1989)

The sulfate aerosol mode radii illustrated in Figure 10 correspond to  $\text{SO}_2$  mass injections of 10 MT (1 MT =  $10^6$  metric tons) (i.e., like El Chichon), and 100 and 200 MT (more like Tambora). The mode radius peaks earlier with larger  $\text{SO}_2$  injections and remains elevated throughout the history of the eruption cloud. In these simulations, the mode radius grew as large as  $0.7 \mu\text{m}$ , which greatly exceeds the ambient mode radius of  $\sim 0.05 \mu\text{m}$ . In the case of large eruptions, the mode radius slowly returns to its ambient value, requiring a period of more than three years. The mode radius is important in determining the rate at which sulfate is removed from the stratosphere. The mass flux is proportional to the fallspeeds of the aerosols multiplied by their mass. Since  $m \propto r^3$  and  $v \propto r^{1-2}$  in the regime of interest, the mass loss rate is,  $\dot{m} \propto r^{4-5}$

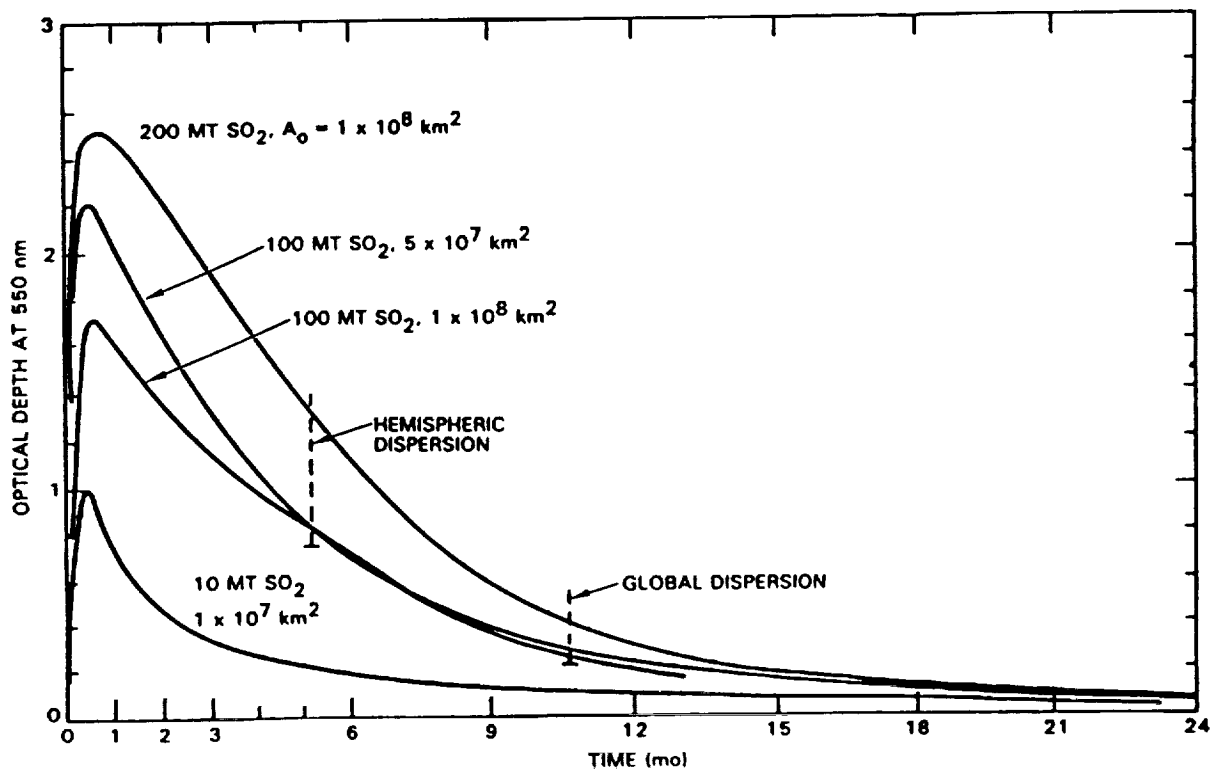


Figure 11. Volcanic aerosol optical depths (zenithal) versus time for the volcanic cloud simulations discussed in Figure 10. Indicated on the figure are the times required model times for the cloud to disperse over a hemisphere or over the globe. (Pinto et al., 1989)

Figure 11 illustrates the evolution of the volcanic aerosol optical depth at mid-visible wavelengths. The optical depth is associated with the scattering of light by the sulfuric acid droplets. At early times, and over limited geographical regions, the optical depths exceed a value of 2. However, after one year of evolution by growth, coagulation and fallout, the average optical depth for even the largest  $\text{SO}_2$  injection has fallen to about 0.5. These results suggest that the nonlinear physical/chemical interactions occurring in volcanic eruption clouds will severely limit the aerosol optical depth that can be maintained over a period of several years -- i.e., the time span required to induce substantial climatic impacts. (Also see the following section)

## Volcanic Aerosol Impact on Radiation and Climate

Many scientists, beginning with Benjamin Franklin, have studied the relation between volcanic explosions and climate/weather change (see Lamb, 1977; Robock, 1981). Existing research indicates that, in the years following a major volcanic eruption, anomalous weather patterns and regional- to global-scale cooling is likely (Robock and Mass, 1982; Rampino et al., 1988). The connection between volcanoes and climate is most directly made through the effect that volcanically-induced sulfate aerosols have on the global radiation budget (see Figure 12). The volcanic aerosols, when formed in the stratosphere where they can be rapidly dispersed around the earth, increase the reflectivity of the atmosphere and reduce incoming solar energy. The aerosols also produce a modest infrared trapping effect, which is not sufficient to reverse the cooling caused by the increased reflectivity (Pollack et al., 1976). The net effect of volcanic emissions of sulfur gases into the stratosphere is an average global cooling of  $\sim 0.5^{\circ}\text{C}$  for 1-3 years. A number of statistical correlations have been uncovered between volcanic eruptions in one year and global cooling in the following years. For example, studies of tree ring records (LaMarche and Hirschboeck, 1983) and similar climatic proxies (Lamb, 1977) support the volcanic cooling hypothesis (Hansen et al., 1978).

The violence of a volcanic eruption is not always directly related to its climatic impact. More important is the quantity of sulfur gases (particularly  $\text{SO}_2$ ) injected into the stratosphere. However, the climate impact of an explosive eruption also appears to be limited to a temperature perturbations of  $\sim 1^{\circ}\text{C}$  even for the largest eruptions. This fundamental limitation may be caused by highly nonlinear physical processes that restrict the buildup and persistence of the aerosol optical depth (Pinto et al., 1989; see Figure 11).



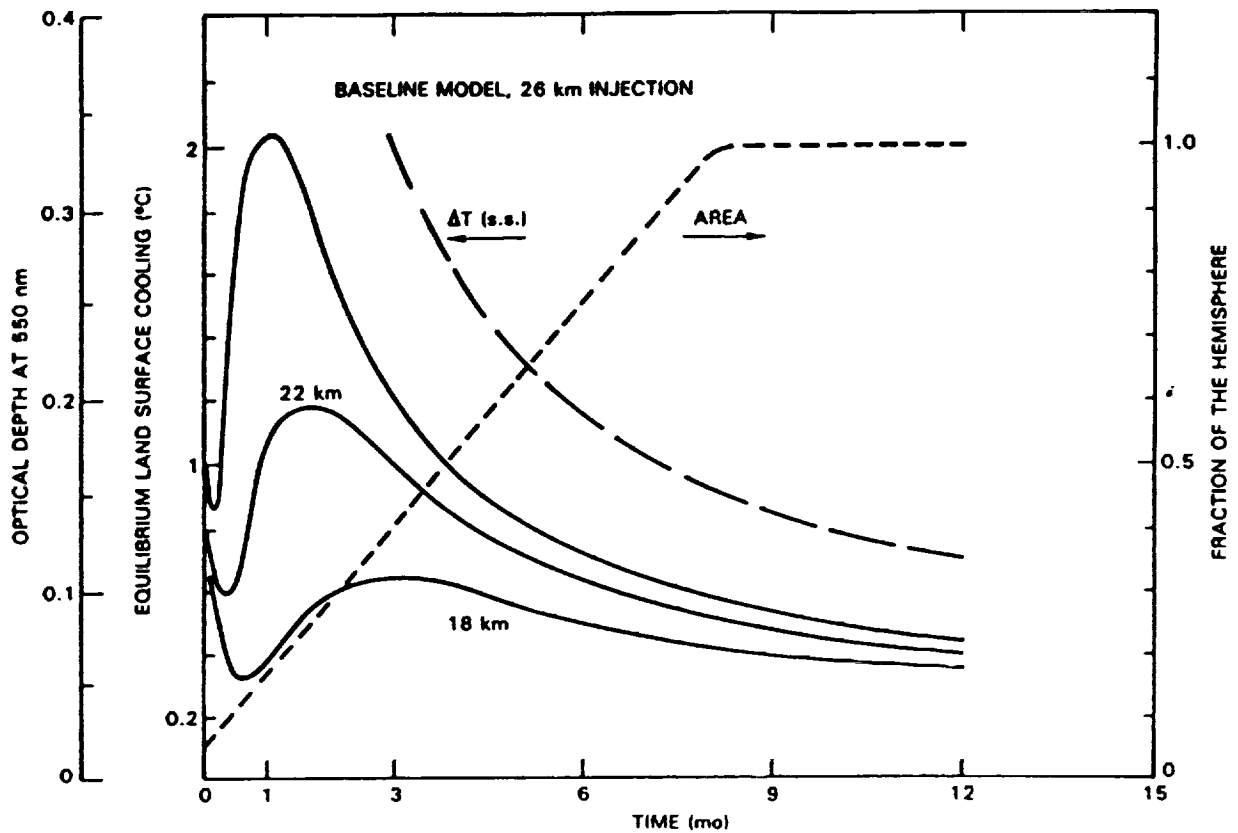


Figure 12. Time-dependent optical depth variations, and corresponding equilibrium surface temperature changes, for an El Chichon-like volcanic eruption of about 10 MT of  $\text{SO}_2$  injected at stratospheric levels up to 26 km, 22 km, and 18 km, respectively, in three simulations. The steady-state (equilibrium) surface temperature variation is only shown for the 26 km injection. The horizontal area of the aerosol cloud -- as represented in the model -- is also given.

The temperature perturbations shown in Figure 12 correspond to the maximum attainable temperature decrease for an optical perturbation that is fixed long enough for the surface/atmosphere system to achieve its new equilibrium state. Thus, it is likely that an eruption such as El Chichon would produce global average coolings of perhaps 0.1-0.2  $^{\circ}\text{C}$ . The climatic impact decreases as the injection height of the precursor gases is lowered from 26 to 18 km (the latter value, for example, characterizes the height of sulfur injection in the Mt. St. Helens eruption).

### **Stratospheric Aerosols as Tropospheric Cloud Condensation Nuclei**

After a major volcanic eruption, the stratospheric aerosols settle into the upper troposphere over a period of several years. These sulfate particles are highly soluble and thus enhance the cloud condensation nuclei (CCN) population of the upper troposphere (Pruppacher and Klett, 1978). It has also been suggested -- but remains speculative -- that such soluble aerosols may provide nuclei for cirrus cloud formation (through spontaneous freezing of supercooled droplets, which then act as ice nuclei). Meteoritic debris particles, which fall through the stratosphere, were once suggested as a source of cloud nuclei, but are unlikely to be important in this regard. Stratospheric particles, acting as nuclei, could modulate the microphysical and radiative properties of upper tropospheric clouds, and hence affect the global climate.

## Polar Stratospheric Clouds

The properties of polar stratospheric clouds have been defined by a decade of satellite observations (McCormick et al., 1982; McCormick and Trepte, 1986, 1987; Hamill and Turco, 1988). On optical and physical evidence, PSC's fall into two broad categories, which we will refer to as Type-I and Type-II PSC's. Type-I PSC's consist of an aerosol haze of micron-sized nitric acid ice particles composed of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  [in roughly a 50/50 mixture by weight, similar to the trihydrate  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ] (Toon et al., 1986; Crutzen and Arnold, 1986). Type-II PSC's are apparently composed of water-ice crystals (Poole and McCormick, 1988; Hamill et al., 1986).

The Type-I PSC's are thought to be the most common form, perhaps accounting for 80-90% of all cloud sightings. These PSC's exhibit an onset at temperatures near 195 K, whereas the denser Type-II PSC's appear to condense at colder temperatures ( $<187$  K) consistent with the measured frost point of water vapor in the polar stratosphere (Poole and McCormick, 1988; Hamill et al., 1988). It should be expected, therefore, that Type-I haze would predominate the totality of cloud observations in the earliest part of the Antarctic winter season, and that the frequency of Type-II clouds would increase with the progression of winter and cooling of upper air layers. On the other hand, the observed dehydration and denitrification of the polar winter stratosphere would, over the course of time, reduce the frequency of cloud formation at specific temperature thresholds. Hence, in the late winter and early spring, PSC's are predicted to dissipate abruptly when sunlight, absorbed by ozone, begins to warm the upper stratosphere (Toon et al., 1989).

The nuclei for nitric acid ice deposition are most likely to be the background sulfuric acid aerosols (Toon et al., 1986). Observational evidence on the extent to which sulfate particles are nucleated in PSCs is mixed. Aircraft measurements taken in the Antarctic ozone hole in September, 1987, suggest that many, if not most, of the sulfate particles may be activated into nitric acid haze particles (Fahey et al., 1989; Poeschel et al., 1989). On the other hand, balloonborne aerosol measurements conducted at McMurdo Station during the same period, and more recent data from the Arctic winter stratosphere, indicate that, although layers of  $\sim 1$  micron-size haze particles are frequently present, on occasion the fraction of the sulfate particles activated into haze may be relatively small (e.g., Hofmann et al., 1989; Hofmann, 1990). If the sulfate particle nucleation is limited to a small fraction of the total number of particles, the resulting low concentration of haze particles will have

important implications for stratospheric denitrification (Salawitch et al., 1988; Toon et al., 1990).

In situ measurements of odd-nitrogen species provide direct evidence for the existence of nitric acid particles in the antarctic winter stratosphere (Fahey et al., 1989; Gandrud et al., 1989; and Pueschel et al., 1989). That evidence is supported by infrared spectroscopic measurements of condensed  $\text{HNO}_3$  (Kinne et al., 1989) and column measurements of depletion of the  $\text{HNO}_3$  vapor column amount (G. Toon et al., 1989; Coffey et al., 1989). In addition, Hanson and Mauersberger (1988a,b), in a series of detailed laboratory studies, have quantified the compositions and vapor pressures of the nitric acid ices under the conditions of interest, and concluded that the nitric acid trihydrate would be the stable form in the stratosphere.

Chemical transformations on PSC ice particles that lead to the formation of the ozone hole are discussed below. Extensive stratospheric ozone depletion may be influenced indirectly by volcanic sulfate aerosols through their role as PSC nuclei. However, sulfate aerosols may have a more direct role in ozone depletion chemistry by catalyzing special reactions (see below).

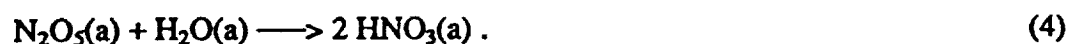
## Aerosol Impact on Stratospheric Chemistry and Ozone

The recent discovery of an ozone "hole" over Antarctica in late austral winter and early spring (Farman et al., 1985) has led to considerable research on the causative processes (e.g., Geophysical Research Letters, Volume 13, Number 12, 1986; Geophysical Research Letters, Volume 15, Number 8, 1988; Journal of Geophysical Research, Volume 94, Numbers D9 and D12, 1989; Geophysical Research Letters, Volume 17, Number 4, 1990). The leading chemical theories assume that "heterogeneous" reactions occur on polar stratospheric cloud (PSC) particles. Laboratory studies show that the ice-catalyzed reaction of HCl with chlorine nitrate ( $\text{ClONO}_2$ ) produces 'active' chlorine. Through known homogeneous photochemical processes, this enhanced activated chlorine can explain most, if not all, of the measured ozone deficits (Solomon et al., 1986; Crutzen and Arnold, 1986; McElroy et al. 1986a,b).

The intense interest in polar stratospheric clouds has led to a new focus on the possible role of other stratospheric aerosols in heterogeneous chemical reactions that might affect stratospheric composition and ozone depletion. An early review of potential heterogeneous reactions on the background sulfate aerosols concluded that such reactions were too slow to be of any significance (Turco et al., 1982). However, that conclusion was based on early measurements of species reactivities on sulfuric acid surfaces that did not match precisely the properties of sulfuric acid particles under stratospheric conditions. New measurements of  $\text{ClONO}_2$  reactivity on such surfaces (Tolbert et al., 1988) indicate a very strong dependence on solution composition, implying a potentially significant chemical impact. Accordingly, a reassessment of potential heterogeneous contributions to global stratospheric chemistry is timely.

## **Heterogeneous Chemical Processes on Stratospheric Aerosols**

The key heterogeneous chemical processes that occur on polar stratospheric cloud particles are:



In these chemical equations, the abbreviation a indicates that the species is adsorbed on the particle surface or absorbed into the particle, and g indicates that the species rapidly desorbs from ice surfaces and is likely to be found in the gas phase. Chlorine activation via reactions 1-3 is very likely to proceed to completion on PSCs, with or without occasional solar illumination, in the early part of polar winter. This conclusion has recently been confirmed by laboratory studies (Moore et al., 1990). Chlorine activation – in combination with denitrification, which is caused by PSC particle sedimentation – results in a perturbed stratospheric composition that is extremely destructive toward ozone. A principal concern for the future is that increasing concentrations of background stratospheric chlorine from chlorofluorocarbons might be extensively activated over the entire globe on sulfate aerosols enhanced by anthropogenic activity (Hofmann, 1989) or generated suddenly by a major volcanic eruption.

## **Anthropogenic Influences on Stratospheric Aerosols**

Human activities can affect the composition and structure of the stratosphere and stratospheric aerosols in a number of ways:

- 1) Carbon dioxide growth leads to a significant cooling of the middle and upper stratosphere thereby altering the dynamics, chemical kinetics and thermodynamics of sulfate particle formation;
- 2) Tropospheric emissions of sulfur-bearing gases such as OCS reach the stratosphere and upon decomposition modify the sulfate layer;
- 3) Direct emissions of sulfur vapors ( $\text{SO}_2$ ) and soot from high-flying aircraft contaminate the natural sulfate layer;
- 4) Fluorocarbons released at the surface diffuse into the stratosphere and are decomposed into chlorine species that are subsequently activated on stratospheric aerosols and attack ozone;
- 5) Direct injection of rocket exhaust particles into the stratosphere, and the increasing rate of ablation of debris from orbiting platforms, enhances the concentration of stratospheric aerosols (Zolensky et al., 1989);
- 6) Other trace gases of tropospheric origin like methane and nitrous oxide are transported into the stratosphere and alter the ambient composition of the air in which stratospheric aerosols form and evolve (e.g., by increasing water vapor concentrations).

Figure 13 illustrates the potential change in the sulfate aerosol size distribution and optical depth resulting from an order-of-magnitude increase in either OCS or  $\text{SO}_2$ . The size distribution is noticeably skewed toward larger particle sizes, which have greater optical activity. The optical depth of these stratospheric aerosols increases substantially (by a factor of almost 5 for the OCS enhancement of a factor of 10), suggesting that their climatic impact could be significant (Turco et al., 1980).

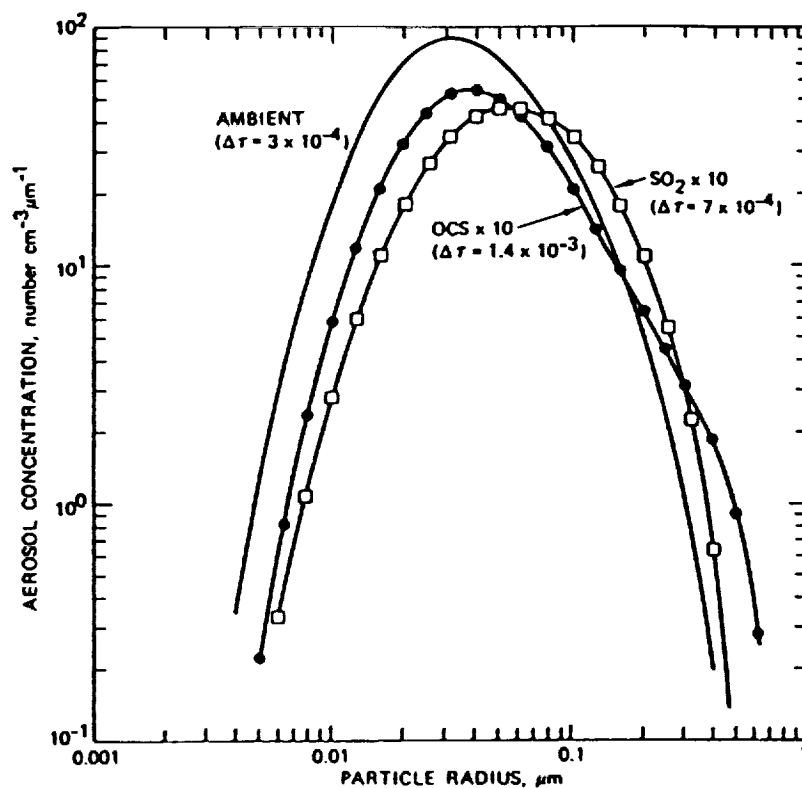


Figure 13. Calculated aerosol size distributions at 20 km for the background stratospheric sulfur gas abundances, compared to the size distributions corresponding to an increase by a factor of 10 in either the OCS or SO<sub>2</sub> ambient abundances. Also indicated in each case are the aerosol optical depths of a layer 1 km thick centered at a height of 20 km.



## Stratospheric Aerosol Observations for Global Change

Stratospheric aerosols participate in global-scale processes that affect the troposphere and biosphere. The presence of aerosols directly influences solar radiation reaching the lower atmosphere and surface, and thus has a role in controlling the climate of earth. If stratospheric aerosols affect the properties of clouds in the upper troposphere, further climatic influences are implied. Sulfate aerosols may also modulate the chemistry of the ozone layer, leading to enhanced ozone depletion following major volcanic eruptions and an increase of harmful ultraviolet radiation at the ground. Stratospheric aerosols are subject to modification by a number of human activities, and these activities therefore may induce climate and other environmental changes. Table 3 lists a number of outstanding scientific questions regarding stratospheric sulfate aerosols -- and volcanic aerosols -- and their effects.

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**Table 3. Outstanding Scientific Issues**

### **Sulfate Aerosols**

- Why is the background sulfate mass increasing?
- How do the sulfate particles act as PSC nuclei?
- Is increased sulfate aerosol reactivity possible, for example, with increasing water vapor?
- What is the chemical nature of the unusual aerosol layers observed near 30-35 km?
- How do stratospheric aerosols affect remote sensing of the upper atmosphere?
- Are stratospheric particles a significant component of the global radiative energy balance under normal conditions, and thus of global climate change?

### **Volcanic Particulates**

- What are the types and frequencies of volcanic eruptions that produce global effects?
- What is the injection efficiency of SO<sub>2</sub>, HCl, H<sub>2</sub>O and other gases?
- Are there strong non-linear limits to the global effects of volcanic injections?
- What is the precise composition of volcanic aerosols for heterogeneous chemistry?
- Do volcanic aerosols act as nuclei for the formation of cirrus in the upper troposphere?
- Is there a measurable effect of volcanic eruptions on climate, or is the effect illusory?
- Do volcanic eruptions affect tropospheric phenomena such as El Nino?
- What has been the role of ancient volcanic eruptions on the course of geological/biological evolution?
- Can volcanic eruptions affect stratospheric ionization, conductivity and electric fields?

To be more certain of the possible connections between the stratosphere and troposphere that involve stratospheric aerosols and that have global change implications, specific scientific programs could be developed:

1) Volcanic aerosol studies: A program should be established to delineate the connection between volcanic emissions, aerosol formation and dispersion, and radiative/climatic impacts of volcanic eruptions; these studies could in part be carried out using the existing data base for the El Chichon eruption of 1982, although the project would aim toward collecting new data -- particularly through long-term satellite observations -- on future eruptions;

2) Aerosol heterogeneous chemistry studies: Accurate laboratory studies on the reactivity -- particularly the chlorine reactivity -- of sulfate (sulfuric acid) aerosols should be carried out under realistic stratospheric conditions; as opportunities arose, in situ chemical perturbations associated with enhanced sulfate aerosols could be studied directly (e.g., following a volcanic eruption, or in a planned sulfur release);

3) Predictive model development: Theoretical models capable of predicting the effects of volcanic eruptions and various human activities on stratospheric aerosols, upper tropospheric aerosols, the global radiation budget and climate should be developed; such models would be global in scale -- optimally three-dimensional -- and include accurate treatments of the appropriate dynamical, photochemical, microphysical and radiative processes;

4) Global aerosol monitoring program: A global monitoring program for stratospheric aerosol trends -- particularly trends that may be associated with anthropogenic emissions but also transients associated with volcanic eruptions -- could be built upon existing and planned satellite and lidar measurement projects; in situ measurements would be necessary for calibration and detailed microphysical/radiative/chemical definition of the aerosols over time.

Finally, the recent conclusions of the Ozone Trends Panel (Watson et al., 1990) on the roles of stratospheric aerosols in the collection of data from space -- particularly data on ozone abundances -- are briefly stated in Table 4.

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**Table 4. Stratospheric Aerosol Impact on Remote Sensing of  
the Upper Atmosphere (Ozone Trends Panel Report)**

Ozone satellite observations (SBUV) suffer minimal degradation, with care required during periods of stratospheric disturbance by volcanic eruptions.

Umkehr ozone measurements suffer major perturbations during periods when the stratospheric aerosols are enhanced by volcanic activity.

Stratospheric aerosol monitoring for radiative transfer compensation of remotely-sensed data and for long-term trends is recommended.

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